

UNCLASSIFIED

AD NUMBER	
AD331340	
CLASSIFICATION CHANGES	
TO:	unclassified
FROM:	confidential
LIMITATION CHANGES	
TO:	Approved for public release, distribution unlimited
FROM:	Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 15 MAY 1962. Other requests shall be referred to Naval Ordnance Lab., White Oak, MD.
AUTHORITY	
31 May 1974, DoDD 5200.10; USNSWC ltr, 7 Oct 1974	

THIS PAGE IS UNCLASSIFIED

AD 331 340

*Reproduced
by the*

**ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA**

NCY



NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

NOLTR 62-73

921340

THE RELATIONSHIP OF SENSITIVITY WITH
STRUCTURE OF ORGANIC HIGH EXPLOSIVES.
II. POLYNITROAROMATIC COMPOUNDS (C)

- PREPARED TO ASTIA
BY THE UNITED STATES NAVAL ORDNANCE LABORATORY
- ☐ All other restrictions
 - ☐ For release to Military and Government Agencies only.
 - ☒ Approval by Bureau required for release to contractors.
 - ☐ Approval by Bureau required for all subsequent release.

NOL

15 MAY 1962

UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

NOTICE: This material contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C. Sections 793 and 794, the transmission or revelation of which in any manner to an unauthorized person is prohibited by law.

NOLTR 62-73

Doc
Unclassified

ASTIA

AUG 30 1962

**Best
Available
Copy**

THE RELATIONSHIP OF SENSITIVITY WITH STRUCTURE OF
ORGANIC HIGH EXPLOSIVES. II. POLY-NITROAROMATIC
COMPOUNDS (C)

Prepared by: Mortimer J. Kamlet
Darrell V. Sickman

Approved by: DARRELL V. SICKMAN, Chief
Organic Chemistry Division

ABSTRACT: The impact sensitivity of an organic high explosive is considered to be primarily a function of its thermal decomposition rate. Classes of compounds with similar structures, and thus assumed to have similar mechanisms of thermal decomposition, show a linear relationship between their impact sensitivity and a defined quantity called "oxidant balance" derivable from the molecular composition. Different structural classes differ in their sensitivity-oxidant balance relationships, i.e., polynitroaromatic compounds with alpha CH groups are more sensitive as a class than those lacking this feature.
(C)

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, SILVER SPRING, MARYLAND

NOLTR 62-73

15 May 1962

This report extends the relationships first described in NAVORD Report (NOL) 6126 to several new classes of compounds. Sensitivity-structure relationships such as those herein described have helped provide a new direction for a synthetic program toward improved performance explosives which may be used with greater safety. The work described in this report was performed under Task No. RUME 3E 000/PA017, Desensitization of Explosives.

W. D. COLKMAN
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

CONFIDENTIAL

TABLE OF CONTENTS

	Page
INTRODUCTION	1
DISCUSSION	3
EXPERIMENTAL	13
ACKNOWLEDGEMENTS	14
REFERENCES	15

ILLUSTRATIONS

TABLE I	Impact Sensitivity and OB_{100} of Nitro- aromatic Explosives	4
TABLE II	Impact Sensitivities of Polynitroalkyl Polynitroaromatics	11
FIGURE 1	Impact Sensitivity of Polynitroaromatics as a Function of OB_{100}	5

INTRODUCTION

The many obscure factors which influence the sensitivity of high-energy compounds have long been of concern to the explosives chemist. The first paper of this series described a relatively recent approach to this problem at NOL (1). The reactions governing the sensitivity of polynitroaliphatic explosives were considered in much the same manner as the organic chemist classically studies any reaction, i.e., by determining the effect of structure on reactivity. We wish now to describe a similar approach as it applies to several types of polynitroaromatic explosives.

The impact test is by far the most common of the many means of evaluating the sensitivity of solid explosives. In this test successive samples of the explosive are subjected to hammer blows caused by a standard weight falling from heights varied in a systematic manner. As carried out at NOL, the technique is a modification of that developed by Eyster and Davis (2) at the Explosives Research Laboratory, Bruceton, Pa., during World War II. The salient features which distinguish the ERL-NOL machine and method from other such tests are the particular tool design, the criterion of explosion, the use of flint paper under the sample, and the statistical procedure used to conduct the experiment and reduce the data.

The sensitivity is reported as that height which has a 50% probability of causing an explosion. Because the machine can distinguish between explosives with 50% heights of 15 and 20 cm about equally as well as between 150 and 200 cm, the logarithm of the 50% height is considered to be the best measure of impact sensitivity. Impact sensitivities (or 50% heights) for some standard explosives on the NOL machine are: TNT, 160 cm; tetryl, 32 cm; RDX, 24 cm; PFTN, 13 cm.

The test, which has the advantage of requiring only 35 mg of material per trial, may be carried out rapidly and conveniently. It has proved to be reasonably successful in separating high explosives into classes with generally similar handling hazards. The machine, however, has neither the resolution nor the reproducibility desired of a research tool and only limited reliability may be attributed to any individual impact result. TNT, the standard used to calibrate the machine, illustrates the poor reproducibility. Occasional twenty-five-shot determinations on twice-recrystallized material have given 50% heights ranging from below 100 cm to above 250 cm. Such variations have

been attributed to operator technique, particle size distribution in the sample, atmospheric conditions (humidity, etc.) and multifold other causes.

In view of the uncertainty associated with individual results and the possible secondary effects of other properties, it was felt that any correlation of impact sensitivity with structure would necessarily depend on a large body of data determined for classes of chemically related compounds. It was hoped that despite doubtful accuracy of the individual determinations, a plot of the data as a function of the structural parameter chosen for comparison would show the data points distributing about a "true trend". This trend might then serve as a tool for predicting variation of impact behavior with the chosen parameter. It was fortunate that the large body of impact sensitivity information required had already been assembled at this laboratory over the years (3) and that a majority of the determinations had been made by the same competent operator.

A convenient structural parameter chosen for comparison was oxidant balance (OB_{100}), a term which we have defined as the number of equivalents of oxidant per hundred grams of explosive above the amount required to burn all carbon to carbon monoxide and all hydrogen to water (1). In calculating OB_{100} an atom of oxygen represents two equivalents of oxidant, an atom of hydrogen one equivalent of reductant and an atom of carbon two equivalents of reductant. Since a "dead-weight" carboxyl group would otherwise increase OB_{100} , two equivalents of oxidant per mole are subtracted for each such group in the molecule*.

*Oxygen atoms in ketone, aldehyde, ether and hydroxyl groups, although contributing little to heat of detonation are included in the oxidant portion of the molecule in calculating the arbitrarily defined OB_{100} . OB_{100} differs from classical "oxygen balance" in that the latter is expressed as a percentage and incorporates no correction for dead-weight carboxyl groups.

For C-H-N-O explosives, the applicable equation is,

$$OB_{100} = \frac{100 (2 n_O - n_H - 2 n_C - 2 n_{COO})}{\text{Mol. Wt.}} \quad (1)$$

where n_O , n_H and n_C represent the number of atoms of oxygen, hydrogen and carbon in the molecule and n_{COO} is the number of carboxyl groups. For explosives balanced to the carbon monoxide level, $OB_{100} = 0$; at the carbon dioxide level, $OB_{100} = ca + 2.5$. Values of OB_{100} are additive for mixtures of explosives or for explosive plus non-explosive diluent.

DISCUSSION

Impact sensitivities of thirty-eight polynitroaromatic and nitroaromatic-nitroaliphatic explosives are listed in Table I together with molecular formulas, molecular weights, molar oxidant balances and values of OB_{100} . These compounds have been divided into two classes, the basis for the division being the presence or absence of a hydrogen atom on a carbon alpha to the ring. The reason for this criterion of distinction will be discussed below.

Logarithmic 50% impact height is plotted as a function of OB_{100} in Figure 1. If all data points are considered equally, the plot shows a general increase in impact height with decreasing OB_{100} , but the band within which all points fall is rather broad. Sensitivities vary from 13 to 24 cm at $OB_{100} = ca +1$, from 21 to 73 cm at $OB_{100} = ca 0$ and from 52 to >320 cm, the top of the scale, at $OB_{100} = ca -2$. No quantitative relationship is evident.

If the distinction between classes is now taken into account, some regularities begin to appear. Twelve of the thirteen compounds which have a hydrogen atom on an alpha carbon show impact sensitivities toward the lower portion of the broad band; twenty-four of the twenty-five lacking this linkage lie in the upper portion. Indeed, if the categories are considered separately, most of the points seem to cluster about individual straight lines.

If, in the light of the inexactness of the impact machine, this apparent separation of the data points is to be ascribed

TABLE I
IMPACT SENSITIVITY AND OB₁₀₀ OF NITROAROMATIC EXPLOSIVES

No	Compound	Mol. Formula	Mol. Wt.	OB ₁₀₀	OB _{50%} , cm.
	A. Compounds with no alpha carbon-hydrogen linkage.				
1.	2,3,4,5,6-pentanitroaniline	C ₆ H ₃ N ₅ O ₁₁	332	+6	+1.88
2.	2,2,2-trinitroethyl 2,4,6-trinitrobenzoate	C ₉ H ₃ N ₉ O ₁₄	420	+4	+0.95
3.	2,4,6-trinitroresorcinol	C ₆ H ₃ N ₃ O ₉	245	+1	+0.41
4.	2,3,4,6-tetranitroaniline	C ₆ H ₂ N ₄ O ₁₀	273	+1	+0.37
5.	2,2,2-trinitroethyl 3,5-dinitrosalicylate	C ₁₀ H ₃ N ₅ O ₁₃	351	+1	+0.26
6.	2,4,6-trinitroresorcinol 3,5-dinitrobenzoate	C ₁₂ H ₃ N ₇ O ₁₅	375	-1	-0.28
7.	picric acid	C ₆ H ₃ N ₃ O ₇	229	-1	-0.44
8.	2,4,6-trinitro-3-aminophenol	C ₆ H ₃ N ₃ O ₇	244	-2	-0.81
9.	2,2',4,4',6,6'-hexanitrobiphenyl	C ₁₂ H ₃ N ₆ O ₁₂	424	-4	-0.54
10.	2,4,6-trinitrobenzoic acid	C ₇ H ₃ N ₃ O ₈	257	-3	-1.12
11.	2,2-dinitropropyl 2,4,6-trinitrobenzoate	C ₁₀ H ₃ N ₅ O ₁₃	389	-5	-1.28
12.	1,3,5-trinitrobenzene	C ₆ H ₃ N ₃ O ₆	213	-3	-1.46
13.	2,4,6-trinitrobenzonitrile	C ₇ H ₂ N ₃ O ₆	238	-4	-1.68
14.	picramide	C ₆ H ₃ N ₃ O ₆	238	-4	-1.75
15.	4,6-dinitroresorcinol	C ₆ H ₃ N ₂ O ₆	200	-4	-2.00
16.	2,4-dinitroresorcinol	C ₆ H ₃ N ₂ O ₆	200	-4	-2.00
17.	2,4,6-trinitroanisole	C ₇ H ₂ N ₃ O ₇	243	-5	-2.06
18.	1,3-dimethoxy-2,4,6-trinitrobenzene	C ₈ H ₂ N ₃ O ₈	273	-7	-2.56
19.	3-methoxy-2,4,6-trinitroaniline	C ₈ H ₂ N ₃ O ₈	273	-6	-2.32
20.	1,3-diamino-2,4,6-trinitrobenzene	C ₆ H ₂ N ₅ O ₆	243	-5	-2.06
21.	2,2',4,4',6,6'-hexanitrodiphenylamine	C ₁₂ H ₂ N ₆ O ₁₂	439	-5	-1.14
22.	2,4,6-trinitrochlorogluconol	C ₆ H ₂ N ₃ O ₉	261	+3	+1.15
23.	3-hydroxy-2,2',4,4',6,6'-hexanitrobiphenyl	C ₁₂ H ₂ N ₆ O ₁₄	440	-2	-0.45
24.	dipicric acid	C ₁₂ H ₂ N ₆ O ₁₄	456	0	0.00
25.	3,3'-diamino-2,2',4,4',5,5',6,6'-hexanitrobiphenyl	C ₁₂ H ₂ N ₈ O ₁₂	454	-6	-1.32
	B. Compounds with alpha carbon-hydrogen linkage				
26.	1-(2,2,2-trinitroethyl)-2,4,6-trinitrobenzene	C ₉ H ₃ N ₉ O ₁₃	376	+4	+1.07
27.	1-(3,3,3-trinitropropyl)-2,4,6-trinitrobenzene	C ₉ H ₃ N ₉ O ₁₃	390	0	0.00
28.	1-(2,2,2-trinitroethyl)-2,4-dinitrobenzene	C ₈ H ₃ N ₅ O ₁₀	331	-1	-0.37
29.	2,4,6-trinitrobenzaldehyde	C ₇ H ₂ N ₃ O ₇	241	-3	-1.24
30.	2,2',4,4',5,5',6,6'-hexanitrobiphenyl	C ₁₂ H ₂ N ₆ O ₁₂	452	-12	-2.64
31.	TNT	C ₇ H ₅ N ₃ O ₆	227	-7	-3.08
32.	2,4,6-trinitrobenzyl alcohol	C ₇ H ₄ N ₃ O ₇	243	-5	-2.06
33.	2,4,6-trinitrobenzaldehyde	C ₇ H ₃ N ₃ O ₇	256	-4	-1.56
34.	2,4,6-trinitro-m-cresol	C ₇ H ₃ N ₃ O ₇	243	-5	-2.06
35.	3-methyl-2,2',4,4',6,6'-hexanitrobiphenyl	C ₁₃ H ₃ N ₆ O ₁₂	438	-8	-1.81
36.	3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl	C ₁₄ H ₃ N ₆ O ₁₂	452	-12	-2.64
37.	3-methyl-2,2',4,4',6-pentanitrobiphenyl	C ₁₃ H ₄ N ₅ O ₁₀	393	-13	-3.30
38.	3,5-dimethylpicric acid	C ₈ H ₄ N ₃ O ₇	257	-9	-3.50

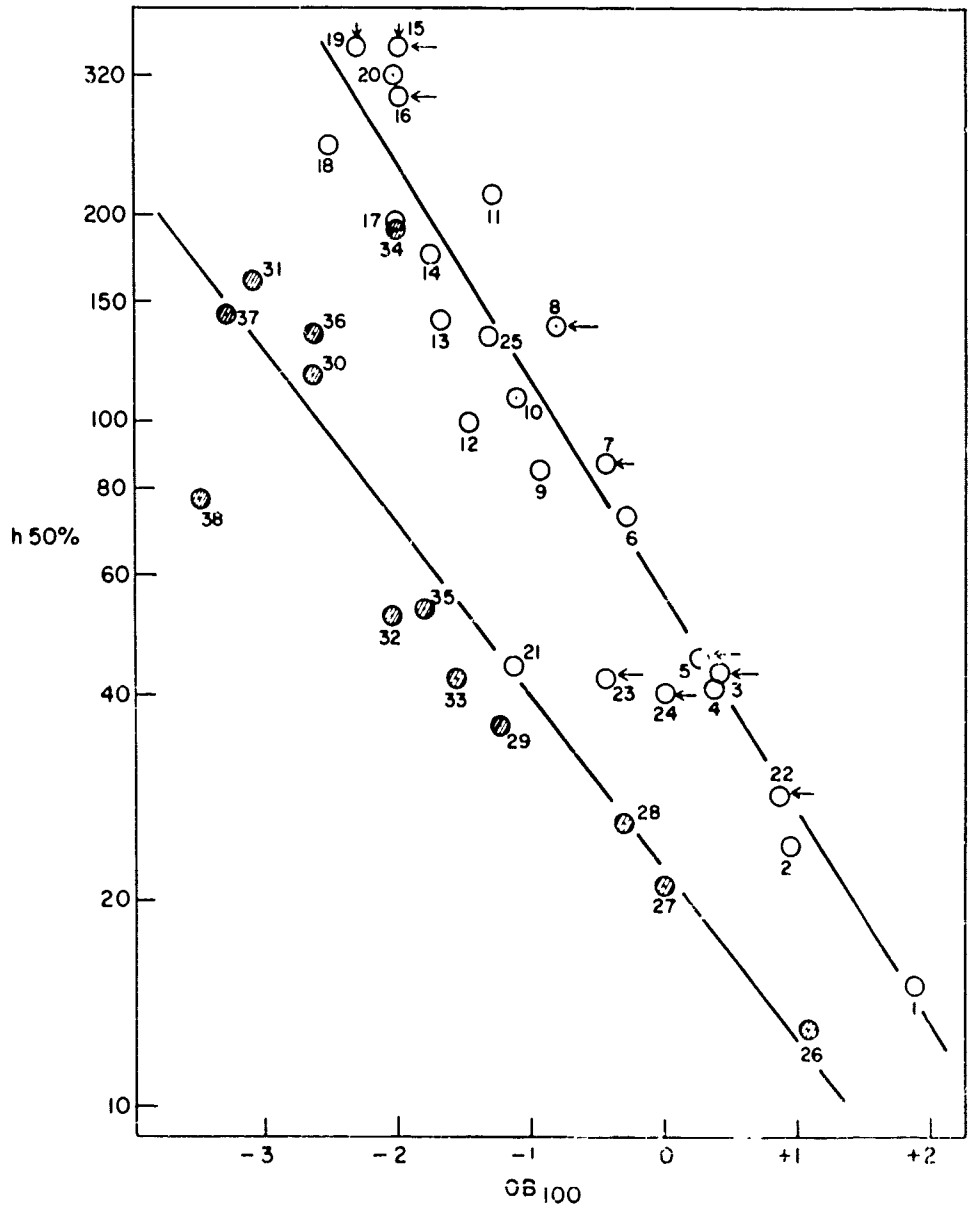


FIG 1 IMPACT SENSITIVITY OF POLYNITROAROMATICS AS A FUNCTION OF OB₁₀₀

to differences in chemical structure, a stronger case can be made if some independent or a priori basis for the separation of the compounds into the two classes is first demonstrated. For this purpose it is necessary to consider the phenomena occurring under the impact hammer in a more detailed manner.

The impact explosion of a high explosive is not a stable detonation. This can be demonstrated by considering the damage to impact tools produced by primary as compared with high explosives. The less powerful primaries, which are believed to detonate, do far more severe damage than the more powerful high explosives. Furthermore, while products of detonation are primarily water, nitrogen and the carbon oxides, analyses of products of impact explosions show relatively large amounts of nitrogen oxides and simple organic molecules such as formaldehyde (4). This suggests that the impact explosion of a high explosive is a phenomenon resembling more closely a relatively low-temperature thermal decomposition than a detonation. It further suggests that reaction kinetics, which do not affect the velocities of stable detonations, may play an important part under the impact hammer.

Groups working with Bowden (5) and Ubbelohde (6) have devoted considerable attention to the mechanism of initiation of explosion by impact. Bowden has proposed that initiations stem from "hot spots" in the explosive mass formed by a number of possible routes including adiabatic compression of entrapped gases, viscous heating and frictional heating. He has concluded that to cause fires in pentaerithritol tetranitrate and nitroglycerine, these hot spots must reach temperatures in the order of 400-500°.

The birth of hot spots and their development into explosions may be governed by a wide variety of physical and chemical properties. In addition to the kinetics of the initial thermal decomposition reaction, these may include (a) the heat evolved in the decomposition reaction, (b) the heat capacity, (c) thermal conductivity and (d) latent heats of fusion and evaporation of the explosive, (e) crystal hardness, (f) crystal shape, etc. In the case of liquids, vapor pressure and dissolved gases may also be significant.

By limiting correlations to solid explosives and by proper design of the impact test, the contributions of several of these properties to sensitivity may be minimized. Thus resting the samples on flint paper is thought to submerge the effects of

crystal hardness and crystal shape. The formation of hot spots is governed more by the physical properties of the sandpaper than by those of the explosive and many differences between polymorphs which are discernible on bare tools can no longer be observed.

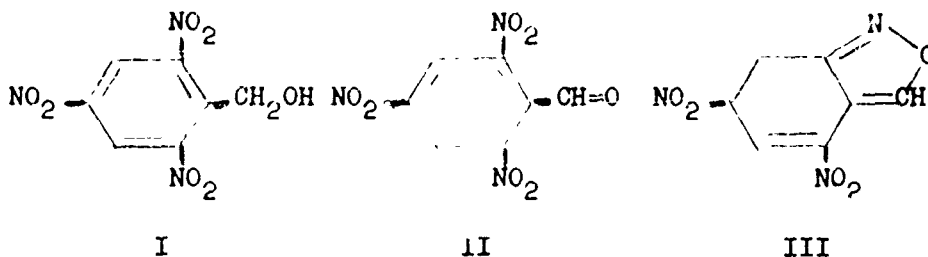
Other properties such as (b), (c) and (d) may differ from explosive to explosive but, if consideration is limited to organic compounds, the range of variation is small. The variation in heat evolved is also relatively small among organic self-explosives. The range 300-1500 calories per gram covers thermal decompositions, low-order explosions and full-scale stable detonations.

Parameters governing rates of thermal decomposition, however, are subject to far greater variation among the types of compounds being considered. Activation energies ranging from 30 to 50 kcal per mole and pre-exponential factors from 10^{12} to 10^{20} sec.⁻¹ have been reported (7). It would seem therefore that, although the part played by other properties may not be ignored, the most likely correlations with impact sensitivity would necessarily depend on chemical reactivity in the classical sense.

This view has recently been corroborated in a convincing manner by Wenograd's experimental measurements of initiation delays in thermal explosions as a function of temperature (7). He found that the temperature at which an explosion would occur within a time comparable to the interval available under the impact hammer varied greatly among explosives. He then demonstrated a direct relationship between these temperatures and measured impact sensitivities, showing that he had, in effect, simulated an impact explosion by a rate measurement.

With the above background, the question now to be considered is whether the separation of data points in Figure 1 is simply an accidental consequence of the vagaries of the impact machine or whether it is the result of some more fundamental chemical difference between the two classes of compounds being examined. Evidence in this regard has been obtained from a study of the products of thermal decomposition of TNT by Dacons and co-workers at NOL. The results of this investigation have been reported in detail in a separate publication (8) but the information which is germane to the present discussion may be summarized as follows.

Twenty-gram samples of TNT, held at 210° in lightly stoppered tubes, were generally found to catch fire within sixteen hours. Samples held for similar periods at 200°C did not ignite, but gave evidence of considerable thermal decomposition. Separation of unreacted TNT from decomposition products by column chromatography was relatively simple and showed that 20 to 30% of the TNT had been consumed. Further separation of the decomposition products was far more difficult, successive rechromatographing indicating the presence of at least twenty and possibly more than fifty discrete zones, each one due to at least one separate chemical entity. The number of zones observed suggested that TNT did not decompose by a single stepwise route, but rather that the detailed decomposition mechanism involved a number of simultaneous routes. Among the major decomposition products isolated, purified and identified were 2,4,6-trinitrobenzyl alcohol (I), 2,4,6-trinitrobenzaldehyde (II) and 4,6-dinitroanthranil (III).



These results indicate that at 200° the thermal decomposition may occur by both inter- and intramolecular reactions but that, whatever the route, a preferred point of initial attack is the methyl group. It is further likely that this attack occurs by abstraction of a hydrogen atom.

Additional striking evidence of the increased reactivity imparted by a methyl group alpha to a polynitroaromatic ring has been obtained from thermal stability measurements. It has been mentioned that TNT self-ignites between 200 and 210°C. 1,3,5-Trinitrobenzene, on the other hand, is stable for at least three hours at 300°C without appreciable gas evolution or

evidence of thermal degradation*.

The significant difference between the two classes of compounds in Table I is now apparent. A preferred site of initial attack, akin to that in TNT, is available for one group and not for the other. It remains only to demonstrate that similar mechanisms may apply in the 250 microsecond thermal decompositions under the impact hammer as in the 16 hour thermal decomposition at 200°, and in this regard it is profitable to refer again to Wenograd's observations (7). The thermal-explosion-initiation-delay measurements were carried out at temperatures ranging from below 300° to above 1200°. Plots of logarithmic time delay as a function of reciprocal temperature showed no pronounced changes in slope in the temperature ranges studied. These were 300-500° for PETN, 500-600° for di(β-nitroxyethyl)nitramine, 500-800° for TNT and 300-1300° for tetryl. Although of limited precision, these results confirm that, for these compounds at least, there were probably no profound changes in mechanism over rather broad temperature spans.

The plots in Figure 1 show a surprisingly linear relationship between $\log h_{50\%}$ and OB_{100} for each class of compounds. The data have been subjected to a least-squares treatment in order that these relationships may be described and used as "true trends" rather than to suggest that the correlations are quantitative.

For eleven polynitroaromatic compounds containing the alpha carbon-hydrogen linkage (3,5-dimethypicric acid, No. 38, and 2,4,6-trinitro-m-cresol, No. 34, not included for reasons which will be discussed below), the true trend fits the equation,

$$\log h_{50\%} = (1.34 - 0.25 OB_{100}) \pm 0.08 \quad (2)$$

For the twenty-four polynitroaromatic compounds lacking this linkage (2,2',4,4',6,6'-hexanitrodiphenylamine, No. 21, has been excluded and an arbitrary value of 350 cm adopted for the compounds firing off-scale), the applicable equation is

$$\log h_{50\%} = (1.74 - 0.31 OB_{100}) \pm 0.09 \quad (3)$$

* Indeed, trinitrobenzene is so stable at 260° that it may be used as solvent in determining gas evolution from solution by other thermally stable explosives at this temperature (9).

In the former instance the term "true trend" is intended to imply a similarity in decomposition mechanism or position of initial attack for all members of the series. The latter group, however, is of far more variegated structure and, from considerations of classical reactivity, a number of widely differing decomposition mechanisms would be expected to apply. The use of a single true trend to describe the impact behavior of these compounds is simply a reflection of our lack of confidence in the resolution of the impact machine. One can, nevertheless, use the latter true trend as a base with which the behavior of any sub-group may be compared.

Thus in Figure 1 a further sub-trend may be discerned if the nine nitrophenol derivatives (compounds 3, 5, 7, 8, 15, 16, 22, 23, 24, indicated by horizontal arrows in the plot) are considered separately. This sub-trend apparently shows a greater slope relative to the overall true trend. The apparent self-consistency, coupled with the fact that the only members of the first group which fell badly out of line were also nitrophenols, lead us to believe that the indicated change in slope is not coincidental.

Although it is possible that the method of calculating OB_{100} wherein phenolic oxygen is considered equivalent to nitro oxygen is partially responsible, it seems firmly established that phenolic oxygen does have some effect in increasing sensitivity. Compare, for example, 1,3,5-trinitrobenzene (100 cm), picric acid (87 cm), 2,4,6-trinitroresorcinol (43 cm) and 2,4,6-trinitrophenol (27 cm); hexanitrobiphenyl (85 cm), hydroxyhexanitrobiphenyl (42 cm) and dihydroxyhexanitrobiphenyl (40 cm); 2,2,2-trinitroethyl 3,5-dinitrobenzoate (73 cm), and 2,2,2-trinitroethyl 3,5-dinitrosalicylate (45 cm); picramide (177 cm) and 2,4,6-trinitro-3-aminophenol (138 cm). In these comparisons the average $\Delta(\log h_{50\%}) / \Delta(OB_{100})$ due to the hydroxyl groups is -0.30. This is not too far different from the -0.31 slope in the overall $\log h_{50\%}$ vs OB_{100} plot.

We had considered modifying equation 1 to give less relative weight to non-nitro oxygens as, for example, by subtracting 0.5 to 1.0 equivalents of oxidant per mole for each such atom.

In view of the above admittedly surprising result and considering the poor resolution of the impact machine, we do not now feel that such a complicating refinement is warranted.

Sensitivities of compounds containing both polynitroaromatic and polynitroaliphatic moieties were of some interest. In the first paper of this series (1) was reported the impact behavior of thirty-three polynitroaliphatic compounds containing nitro groups bonded only to carbon. For this group the applicable true trend fits the equation,

$$\log h_{50\%} = (1.74 - 0.28 OB_{100}). \quad (4)$$

Since equations (3) and (4) predict closely comparable sensitivities at oxidant balances near zero, it is impossible to judge whether the esters 2,2,2-trinitroethyl 2,4,6-trinitrobenzoate, 2,2,2-trinitroethyl 3,5-dinitrosalicylate, 2,2,2-trinitroethyl 3,5-dinitrobenzoate and 2,2-dinitropropyl 2,4,6-trinitrobenzoate (comps. 2, 5, 6 and 11) should be considered with the applicable nitroaliphatic or nitroaromatic series. In the case of compounds 26, 27 and 28, the appropriate equations predict widely differing sensitivities (Table II).

TABLE II

IMPACT SENSITIVITIES OF POLYNITROALKYL POLYNITROAROMATICS

No.	Compound	Predicted Equation 2	Predicted Equation 4	Measured
26.	1-(2,2,2-trinitroethyl)- 2,4,6-trinitrobenzene	12 cm	28 cm	13 cm
27.	1-(3,3,3-trinitropropyl)- 2,4,6-trinitrobenzene	22 cm	55 cm	21 cm
28.	1-(2,2,2-trinitroethyl)- 2,4-dinitrobenzene	26 cm	65 cm	31 cm

Little doubt can exist that these compounds should be considered with the more sensitive class and that their decomposition mechanisms are more closely akin to that of TNT than of polynitroaliphatic compounds.

Table II illustrates a conclusion which will be extended in subsequent papers of this series. If a compound has structural features common to more than one sensitivity category, its impact behavior will normally conform most closely with the true trend of the most sensitive.

Of the thirty-eight compounds considered, three stand out as anomalous. Hexanitrodiphenylamine (No. 21) and 3,5-dimethylpicric acid (No. 38) are definitely more sensitive and 2,4,6-trinitro-m-cresol (No. 34) is definitely less sensitive than the applicable equations would predict.

These serve to emphasize an important consequence of the correlation of molecular structure with sensitivity which we believe we have established. Abnormalities caused by unexpectedly large secondary effects or, as we feel is here the case, by unexpected reactivity or lack of reactivity are unmistakably thrust forward. Useful as is the ability to predict normal sensitivity behavior, the greatest promise of widening our understanding of the reactivity of high energy compounds lies in the ability to isolate and study such exceptional behavior.

The extreme sensitivity of dimethylpicric acid may provide such an insight. Trinitrophenylglucitol and TATB are the only other hexa-substituted benzenes for which impact data are available and in the latter compounds strong hydrogen bonding forces may favor coplanarity of the nitro groups. Spectral evidence is available that, although the nitro groups in monomethylpicric acid are still essentially coplanar in solution, in dimethylpicric acid all three nitro groups have been forced out of planarity (10). If a non-coplanar nitro group is a better oxidizing agent toward methyl, or if a non-hydrogen-bonded hydroxyl group is more easily oxidized than methyl*, such behavior is readily rationalized. By an extension of such an argument, if a hydrogen-bonded coplanar nitro group is a poorer oxidizing agent toward methyl than a non-hydrogen-bonded coplanar nitro group, the relative insensitivity of trinitro-m-cresol may be rationalized**.

* For all other phenols in Table I, hydroxyl-to-coplanar-nitro hydrogen-bonding is possible.

** We are satisfied that the high 50% high of this compound is not due to machine error. Additional twenty-five-shot determinations on recrystallized material gave values of 192 and 177 cm.

We are hopeful that more detailed knowledge of the geometry of these structures from a crystal structure program now under way (11), further study of the mechanism and kinetics of thermal decomposition reactions, improved understanding of electronic interactions from absorption spectra studies and other approaches may dovetail into a unified theory of structure, sensitivity and thermal stability. These important properties of high energy organic molecules would thus become as predictable from a priori theory as would their method of synthesis from the more usual principles of organic chemical reactivity.

EXPERIMENTAL

The impact test (2). The impact tools (type 12) consist of a 3.50 inch long striker and a 1.25 inch long anvil machined to 1.25 inches diameter from "Ketos" tool steel and hardened to Rockwell C-60-63. The contacting surfaces are polished. When, after successive repolishing, the length of the striker falls below 3.47 inches it is discarded. A conical heap, comprising about 35 mg of the granular explosive, is centered on the anvil on a piece of 5/0 flint paper. The flat surface of the striker is rested on the sample through a closely fitting guide ring. The striker is then hit by a 2.50 kg. weight dropped from heights which are varied according to the "up-down" experimental design described by Dixon and Massey (12). This design permits the calculation of a height from which drops will cause explosions 50% of the time. The impact sensitivities reported in Table I are 50% heights as generally determined from twenty-five shot sequences. A microphone-actuated noisemeter, set to record sounds louder than a preset intensity, decides whether a given shot has resulted in an explosion. The noisemeter is calibrated at that value which will cause TNT to have a 50% height of 160 cm.

The data. Impact results were included for all available compounds which met the following criteria. The compound (a) was solid at room temperature, (b) contained no heteroaromatic ring such as triazole, tetrazole, etc., (c) contained no acetylenic or azido groups and (d) was not a salt. For inclusion it was also necessary that σ , the logarithm of the standard deviation of the series of measurements, be less than 0.3. A majority of the determinations showed $\sigma = < 0.15$.

Materials were recrystallized until melting points agreed with literature values or until elemental analyses met journal standards. The preparation of compounds which are not routinely available will be described in forthcoming publications from these laboratories.

Acknowledgements.

A technique so readily susceptible to determinational error depends to a very great extent on the operator. The authors acknowledge with gratitude the services of Mrs. Sarah Duck of the Chemical Engineering Division of NOL over the entire ten-year period during which these measurements were made. We wish also to thank Drs. Kathryn G. Shipp, Joseph C. Dacons, Horst Adolph, Thomas N. Hall and Lloyd A. Kaplan and Messers. M. E. Hill and F. Taylor, Jr. for preparing many of the compounds and Drs. J. M. Rosen, J. C. Dacons, J. R. Holden and J. Wenograd for helpful and stimulating discussions.

REFERENCES

1. M. J. Kamlet, NAVORD Report (NOL) 6126, A Correlation of Impact Sensitivities of Explosives with Oxidant Balances, 26 Sep 1958.
2. H. D. Mallory, NAVORD Report (NOL) 4236, The Development of Impact Sensitivity Tests at the Explosives Research Laboratory, Bruceton, Pennsylvania During the Years 1941-1945, 16 Mar 1956.
3. N. D. Mason, G. Svadeba, L. E. Starr, S. F. Duck, G. W. Reynolds and L. D. Hampton, NAVORD Reports 2184, 2433, 2940, 3955, 4058, 4212, 4352, 4394, 4458 and subsequent reports in the series Sensitivity of Explosives to Impact.
4. A. J. B. Robertson and A. D. Yoffee, Nature, 161, 806 (1948).
5. F. P. Bowden and A. D. Yoffee, Initiation and Growth of Explosions in Liquids and Solids, Cambridge University Press, 1952.
6. J. L. Copp, S. E. Napier, T. Nash, W. J. Powell, H. Skelley, A. R. Ubbelohde and P. Woodward, Phil. Trans. Roy. Soc., A-241, 197 (1948).
7. J. Wenograd, Trans. Faraday Soc., 57, 1612 (1961).
8. J. C. Dacons, M. J. Kamlet and D. V. Sickman, NAVORD Report 6831, Thermal Decomposition of TNT, 1 May 1960.
9. Unpublished work of Dr. J. M. Rosen, NOL.
10. C. E. Moore and R. Peck, J. Org. Chem., 20, 673 (1955).
11. J. R. Holden, NOLTR 62-46, The Crystal Structure of 1,3-Diamino-2,4,6-trinitrobenzene, Form I, Mar, 1962.
12. Dixon and Massey, Introduction to Statistical Analysis, McGraw-Hill Book Co., Inc., New York, 1951, Chapter 19.

Distribution

	<u>No.</u> <u>Copies</u>
Chief, Bureau of Naval Weapons, Department of the Navy, Washington 25, D. C.	
Attn: D-1	1
DLI-3	2
RRRE-5	1
RUME-11	1
RUME-323	1
RMMP-21	1
Chief, Office of Naval Research, Washington 25, D. C.	
Attn: Power Branch (Code 429)	2
Dr. Ralph Roberts	1
Chief of Ordnance, Department of the Army, Washington 25, D. C.	
Attn: Technical Library	1
ODTM	1
Chief of Engineers, Department of the Army, Washington 25, D. C.	
Attn: Research and Development Division	1
Commander, Air Force Logistics Command, Wright-Patterson Air Force Base, Dayton, Ohio	
Attn: Technical Library	1
Commander, Naval Ordnance Test Station, China Lake, Calif.	
Attn: Chemistry Research Section	1
Dr. Martin H. Kaufman (Code 4544)	1
Director, Naval Research Laboratory, Washington 25, D. C.	
Attn: Chemistry Division	1
Commanding Officer, Naval Weapons Station, Yorktown, Va.	
Attn: Research and Development Laboratory	1
Commanding Officer, Naval Propellant Plant, Indian Head, Maryland	
Attn: Technical Library	1
Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland	
Attn: Technical Library	2
Armed Services Technical Information Agency, Arlington Hall Station, Arlington 12, Virginia	
Attn: TIPDR	10
Commanding General, Aberdeen Proving Ground, Aberdeen, Md.	
Attn: Ballistics Research Center	1
Corps of Engineers, U. S. Army Engineering Research and Development Laboratories, Ft. Belvoir, Virginia	
Attn: Technical Library	1

Distribution
(Cont'd)

	<u>No.</u> <u>Copies</u>
University of California, Lawrence Radiation Laboratory, P. O. Box 808, Livermore, California	
Attn: Chemistry Division, Dr. Gus Dorough	2
Commander, Naval Ordnance Laboratory, Corona, Calif.	
Attn: Technical Library	1
Hercules Powder Company, Wilmington 99, Delaware	
Attn: Dr. Julius Roth (Contract No. 16129)	1
Commanding Officer, Picatinny Arsenal, Dover, N. J.	
Attn: Chemistry Research Section	1
Commanding General, Redstone Arsenal, Huntsville, Ala.	
Attn: Technical Library	1
Rohm and Haas Research Division	1
Commander, Eglin Air Force Base, Florida	
Attn: PGTRI, Technical Library	1
Director, Los Alamos Scientific Laboratory, P. O. Box 1663, Los Alamos, New Mexico	
Attn: Dr. L. C. Smith	1
Commander, OOAMA, Hill Air Force Base, Utah	
Attn: Air Force Ammunition Services Office	1
Commanding General, Frankford Arsenal, Philadelphia, Pa.	
Attn: Technical Library	1
Aerojet-General Corporation, Azusa, California	
Attn: Dr. J. R. Fischer (Contract Nonr-2655(00)).....	1
Aerojet-General Corporation, Sacramento, California	
Attn: Dr. Marvin H. Gold (Contract Nonr-2655(00)).....	1
American Cyanamid Company (Contract NOW-60-0745-c) P. O. Box 270, New Castle, Pennsylvania	
Attn: L. V. Clark, Director, Explosives Research and Development	1
Director, Advanced Research Projects Agency, Pentagon, Room 3D-159, Washington 25, D. C.	
Attn: Advanced Propellant Chemistry Office	1
Director, Special Projects Office, Department of the Navy, Washington 25, D. C.	
Attn: Technical Library	1
Minnesota Mining and Manufacturing Company 2301 Hudson Rd., St. Paul 19, Minnesota (ARPA Project No. 201-2)	
Attn: Dr. Morton H. Friedman, Central Research Dept. .	1
Thiokol Chemical Corporation, Reaction Motors Division Denville, New Jersey (Contract Nonr 3664(00))	
Attn: Dr. D. D. Perry	1

CATALOGING INFORMATION FOR LIBRARY USE

BIBLIOGRAPHIC INFORMATION

Descriptors		Codes	Descriptors		Codes
Source	NCL technical report	NOLTR	Security Classification and Code Count	Confidential - 18	COL8
Report Number	62-73	620073	Circulation Limitation		
Report Date	15 May 1962	0562	Circulation Limitation or Bibliographic		
			Bibliographic (Suppl., Vol., etc.)		

SUBJECT ANALYSIS OF REPORT

Descriptors		Codes	Descriptors		Codes
Relationship		REL	Decomposition	DECM	
Sensitivity		SENV	Rate	RATE	
Structure		STRC	Oxidant	OXIA	
Explosives		EXPL	Balance	BALN	
Organic		ORGA	Molecular	MOLC	
High		HIGH	Composition	CMPO	
Poly		POYA			
Nitro		NIRO			
Aromatic		AROM			
Compounds		CMPT			
Impact		IMPC			
Thermal		THER			

<p>Naval Ordnance Laboratory, White Oak, Md. NOL technical report 62-73 THE RELATIONSHIP OF SENSITIVITY WITH STRUCTURE OF ORGANIC HIGH EXPLOSIVES. II. POLYNITROAROMATIC COMPOUNDS (C), by Mortimer J. Kamlet and Darrell V. Suckman, 15 May 1962. 15p. tables. BuWeps task RUM 3E 000/PA017. CONFIDENTIAL</p>	<p>Explosives, High - Sensitivity Explosives, High - Thermodynamics Explosives, High - Impact Polynitro compounds Title Kamlet, Mortimer J. Suckman, Darrell V., Jr. author Project</p>	<p>1. Explosives, High - Sensitivity 2. Explosives, High - Thermodynamics 3. Explosives, High - Impact 4. Polynitro compounds I. Title II. Kamlet, Mortimer J. III. Suckman, Darrell V., Jr. author IV. Project Abstract card is confidential</p>
<p>Naval Ordnance Laboratory, White Oak, Md. NOL technical report 62-73 THE RELATIONSHIP OF SENSITIVITY WITH STRUCTURE OF ORGANIC HIGH EXPLOSIVES. II. POLYNITROAROMATIC COMPOUNDS (C), by Mortimer J. Kamlet and Darrell V. Suckman, 15 May 1962. 15p. tables. BuWeps task RUM 3E 000/PA017. CONFIDENTIAL</p>	<p>Explosives, High - Sensitivity Explosives, High - Thermodynamics Explosives, High - Impact Polynitro compounds Title Kamlet, Mortimer J. Suckman, Darrell V., Jr. author Project</p>	<p>1. Explosives, High - Sensitivity 2. Explosives, High - Thermodynamics 3. Explosives, High - Impact 4. Polynitro compounds I. Title II. Kamlet, Mortimer J. III. Suckman, Darrell V., Jr. author IV. Project Abstract card is confidential</p>
<p>Naval Ordnance Laboratory, White Oak, Md. NOL technical report 62-73 THE RELATIONSHIP OF SENSITIVITY WITH STRUCTURE OF ORGANIC HIGH EXPLOSIVES. II. POLYNITROAROMATIC COMPOUNDS (C), by Mortimer J. Kamlet and Darrell V. Suckman, 15 May 1962. 15p. tables. BuWeps task RUM 3E 000/PA017. CONFIDENTIAL</p>	<p>Explosives, High - Sensitivity Explosives, High - Thermodynamics Explosives, High - Impact Polynitro compounds Title Kamlet, Mortimer J. Suckman, Darrell V., Jr. author Project</p>	<p>1. Explosives, High - Sensitivity 2. Explosives, High - Thermodynamics 3. Explosives, High - Impact 4. Polynitro compounds I. Title II. Kamlet, Mortimer J. III. Suckman, Darrell V., Jr. author IV. Project Abstract card is confidential</p>